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金铁锁的两个新三萜皂苷*

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摘要：从石竹科植物金铁锁（*Psammosilene tunicoides* W. C. Wu et C. Y. Wu）根部分离得到4个齐墩果酸型五环三萜皂苷。它们的结构通过波谱和化学方法分别鉴定为：3-O-β-D-galactopyranosyl-(1→2)-β-D-6-O-methylglucuronopyranosyl-quillaic acid **(1)**，3-O-β-D-galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-glucuronopyranosyl-quillaic acid **(2)**，3-O-β-D-galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-6-O-methylglucuronopyranosyl-quillaic acid **(3)**，3-O-β-D-galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-6-O-ethylglucuronopyranosyl-quillaic acid **(4)**。其中1为木鳖子中发现的次甙，3和4为新化合物。**

关键词：金铁锁；石竹科；三萜皂苷
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Two New Triterpenoid Saponins from *Psammosilene tunicoides* *

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Abstract：Four oleanane-type triterpenoid saponins were isolated from the roots of *Psammosilene tunicoides* W. C. Wu et C. Y. Wu. Their structures were elucidated on the basis of spectral and chemical evidence as 3-O-β-D-galactopyranosyl-(1→2)-β-D-6-O-methylglucuronopyranosyl quillaic acid **(1)**，3-O-β-D-galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-glucuronopyranosyl quillaic acid **(2)**，3-O-β-D-galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-6-O-methylglucuronopyranosyl quillaic acid **(3)**，3-O-β-D-galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-6-O-ethylglucuronopyranosyl quillaic acid **(4)**，respectively. Among them，**3** and **4** were new compounds.

Key words：*Psammosilene tunicoides*；Caryophyllaceae；Triterpenoid saponins

Psammosilene tunicoides W. C. Wu et C. Y. Wu (Caryophyllaceae) is often used in Yunnan folk for stopping bleeding，relieving pain and promoting blood circulation (Lan，1976). The crude

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saponins obtained from the plant exhibited pain-relieving and anti-inflammatory activities (Song, 1981). The chemical constituents of this plant had been investigated before (Pu *et al*, 1984; Pu & Zhou, 1987; 1989). In order to search for the active constituents from this genus, we reinvestigated this plant and have reported the isolation and structure elucidation of five triterpenoid saponins in the preceding paper (Zhong *et al*, 2002). This paper provides the structure elucidation of another four oleanane-type triterpenoid saponins (**1 – 4**).

Result and Discussion

Compound **1** was obtained as a white amorphous powder. Its molecular formula was assigned as $C_{43}H_{66}O_{16}$ by HRFABMS showing a molecular ion $[M]^-$ at *m/z* 838.4371 (calcd for $C_{43}H_{66}O_{16}$ *m/z* 838.4322). The ^{13}C NMR spectra revealed six tertiary methyl carbons (δ 10.9, 15.8, 17.5, 27.3, 33.4, 24.9), two olefinic carbons (δ 122.1, 145.3), one carboxylic carbon (δ 180.0), one aldehydic carbon (δ 209.4), one ester carbon (δ 170.4), one methoxy carbon (δ 52.2) and two anomeric carbons (δ 103.3, 106.3). The ^1H NMR spectra showed signals of the corresponding two anomeric protons [δ 4.88 (d, J = 6.8 Hz), 5.20 (d, J = 7.5 Hz)], indicating β-glycosidic linkages. According to the literature, the ^1H and ^{13}C NMR spectral data were identical to those of the degradation product of Lucyoside N from *Luffa cylindrica* Roem (Yoshikawa *et al*, 1991). Therefore, the structure of **1** was determined to be 3-O-β-D-galactopyranosyl-(1→2)-β-D-6-O-methylglucuronopyranosyl quillaic acid.

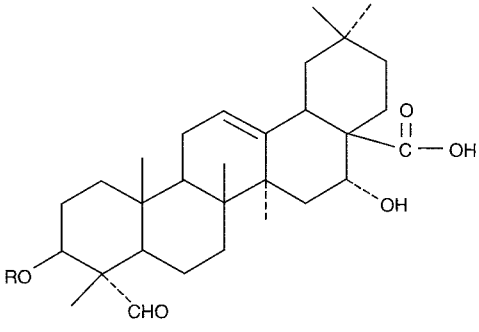
Negative FABMS and ^{13}C NMR spectra of compound **2** suggested the molecular formula $C_{47}H_{72}O_{20}$. Compared to the literature (Guo *et al*, 1998), the structure of compound **2** could be represented as 3-O-β-D-galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-glucuronopyranosyl quillaic acid. Its spectral data were in good agreement with those in the literature.

Compound **3** was isolated as a white amorphous powder. The HRFABMS of **3** gave a $[M-1]^-$ ion at *m/z* 969.4706, in agreement with the molecular fomula $C_{48}H_{74}O_{20}$ (calcd for $C_{48}H_{73}O_{20}$ *m/z* 969.4695). The ^{13}C and ^1H NMR spectra showed signals of three anomeric carbons and the corresponding three anomeric protons [(104.3, 103.8, 105.0; 4.88 (d, J = 6.8 Hz), 5.30 (d, J = 7.6 Hz), 5.54 (d, J = 7.6)], indicating β-glycosidic linkages.

Acid hydrosis of **3** with 5% H_2SO_4-MeOH gave an aglycone which was identified as quillaic acid by comparison of its ^{13}C NMR spectra with reported data (Yoshikawa *et al*, 1991), and glucuronic acid, galactose, xylose (co-TLC with anthentic samples). Sugar proton signals in the ^1H NMR spectra were assigned by ^1H-^1H COSY experiments. Using this technique, the spin-systems starting with the aromeric proton signals could be determined. Thereafter the ^{13}C signals were assigned by the C-H connectivities observed as cross-peaks in the HMQC spectra. Sugar linkages could be determined by the HMBC spectra showing long range correlations between H – 1 of glcUA (δ 4.88) and C – 3 of the aglycone (δ 84.44), H – 1 of gal· (δ 5.30) and C – 2 of glcUA· (δ 75.55), H – 1 of xyl· (δ 5.54) and C – 3 of glcUA· (δ 85.91). Furthermore, the HMBC spectra also showed cross-peaks

between the methoxy group (δ 4.1, s) and C-6 of glcUA· (δ 169.9), indicating the presence of methyl glucuronate. This was also confirmed by the presence of $[M-132-162-176-14]^-$ ion peak at *m/z* 486. Based on the above results, and the assumption that gal·, xyl· and glcUA· are members of the commonly found D-series, the structure of **3** could be deduced to be 3-O-β-D-galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-6-O-methylglucuronopyranosyl quillaic acid.

Compound **4** possessed the molecular formula $C_{49}H_{76}O_{20}$ as determined by HRFABMS showing a $[M-1]^-$ ion at *m/z* 983.4832 (calcd for $C_{49}H_{75}O_{20}$ *m/z* 983.4852). The molecular weight was 14 amu more than that of **3** suggested that **4** contained one additional methene group. Other significant peaks visible at *m/z* 955 $[M-29]^-$, 486 $[M-132-162-176-29]^-$ in the Negative FABMS spectra suggested the elimination of one ethyl and one ethyl glucuronate. Further comparison of the ^1H and ^{13}C NMR spectra of **4** with that of **3** revealed that the two compounds were very similar excepted that the methoxy carbon (δ 52.2) in **3** was replaced by one oxymethene (δ 61.4) and one methyl carbon (δ 14.2) in **4**, confirming the presence of ethyl glucuronate. Hence, the structure of **4** was represented as 3-O-β-D-galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-6-O-ethylglucuronopyranosyl quillaic acid.



R

(1) Me | 6 — GlcUA — 2 — Gal

(2) — GlcUA — 2 — Gal, GlcUA | 3 — Xyl

(3) Me | 6 — GlcUA — 2 — Gal, GlcUA | 3 — Xyl

(4) Et | 6 — GlcUA — 2 — Gal, GlcUA | 3 — Xyl

GlcUA: β-D-glucuronopyranosyl, Gal: β-D-galactopyranosyl

Xyl: β-D-xylopyranosyl

3-O-β-D-galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-glucuronopyranosyl quillaic acid (**2**) (5 mg) and silica gel (500 mg) were added to 10 ml MeOH or 90% EtOH. Then the mixture was heated in a boiling water bath under reflux for 2 h. After filtered the mixture, we checked the filtrate by TLC and did not find **3** or **4** in the solution. So compounds **3** and **4** were natural products in *Psammosilene tunicoides*.

Experimental

General experimental procedures MPs: uncorrected; ^1H NMR, ^{13}C NMR and 2D-NMR spectra were recorded on Bruker AM-400 spectrometer with TMS as internal standard and C_5D_5N as solvent; FABMS data were recorded on a VG Autospec-3000 spectrometer.

Plant material The dried roots of *Psammosilene tunicoides* were purchased from Kunming, Yunnan.

Extraction and isolation The dried roots of *Psammosilene tunicoides* (10 Kg) were extracted with EtOH (90%) for four times under reflux, and the solution was evaporated in *vacuo*. The residue was suspended in acetone to afford crude saponin as a precipitate, which was subjected to silica gel column chromatography, eluting with $CHCl_3$-MeOH-H_2O (8:2:0.2 – 65:35:8) to give two main fractions. The two fractions were further purified on silica gel, RP-18 column to yield (**1**) (65 mg), (**2**) (32 mg), (**3**) (72 mg), (**4**) (25 mg).

Compound **1** White amorphous powder. mp 200 – 205℃. $[\alpha]_D^{20}$ + 15.97° (c = 0.313, CH_3OH). FABMS *m/z*: 838 $[M]^-$ (100), 676 $[M-162]^-$ (35), 485 $[M-H-162-190]^-$ (12); HRFABMS: $[M]^-$ at *m/z*: 838.4371 (calcd for $C_{43}H_{66}O_{16}$, 838.4322). ^1H NMR (C_5D_5N, 400 MHz): δ 5.20 (1H, d, J = 7.5 Hz, Gal – H – 1), 4.88 (1H, d, J = 6.8 Hz, GlcUA – H – 1), 3.78 (1H, m, H – 3), 5.65 (1H, m, H – 12), 9.90 (1H, s, H – 23), 5.25 (1H, br s, H – 16), 1.41 (3H, s, H – 24); ^{13}C NMR data, see Table 1. ^1H and ^{13}C NMR spectral data were identical to the published (Yoshikawa *et al*, 1991).

Compound **2** White amorphous powder. $C_{47}H_{72}O_{20}$. mp 276 – 280℃. FABMS *m/z*: 956 $[M]^-$ (100), 824 $[M-132]^-$ (10), 794 $[M-162]^-$ (8), 662 $[M-132-162]^-$ (5), 486 $[M-132-162-176]^-$ (3); ^1H NMR (C_5D_5N, 400 MHz): δ 5.49 (1H, d, J = 6.5 Hz, Xyl – H – 1), δ 5.29 (1H, d, J = 6.4 Hz, Gal – H – 1), 4.80 (1H, d, J = 6.9 Hz, GlcUA – H – 1), 3.80 (1H, m, H – 3), 5.58 (1H, m, H – 12), 9.86 (1H, s, H – 23), 5.24 (1H, br s, H – 16), 1.35 (3H, s, H – 24); ^{13}C NMR data, see Table 1. ^1H and ^{13}C NMR spectral data were identical to the published (Guo *et al*, 1998).

Compound **3** White amorphous powder. mp 225 – 228℃. $[\alpha]_D^{25}$ + 12.31° (c = 0.325, CH_3OH). FABMS *m/z*: 970 $[M]^-$ (100), 838 $[M-132]^-$ (15), 808 $[M-162]^-$ (20), 676 $[M-132-162]^-$ (8), 486 $[M-132-162-190]^-$ (5); HRFABMS: $[M-1]^-$ at *m/z*: 969.4706 (calcd for $C_{48}H_{73}O_{20}$, 969.4695). ^1H NMR (C_5D_5N, 400 MHz): δ 5.54 (1H, d, J = 7.6 Hz, Xyl – H – 1), 5.30 (1H, d, J = 7.6 Hz, Gal – H – 1), 4.88 (1H, d, J = 6.8 Hz, GlcUA – H – 1), 3.83 (1H, m, H – 3), 5.60 (1H, m, H – 12), 9.87 (1H, s, H – 23), 5.26 (1H, br s, H – 16), 1.41 (3H, s, H – 24); ^{13}C NMR data, see Table 1.

Acidic Hydrohysis of Compound 3 **3** (40 mg) was dissolved in 5% H_2SO_4-MeOH (20 ml) and was heated in a boiling water bath under reflux for 2 h. Water was added (10 ml), and then MeOH was evaporated off in *vacuo*. The aqueous solution was extracted with $CHCl_3$ (40 ml × 3) and concentrated in *vacuo* to afford **3a** (15 mg). The aqueous layer was neutralized with Ba_2CO_3 and filtered, then the filtrate was concentrated to dryness to give a sugar fraction, which contained D-glucuronic acid, D-galactose, D-xylose, as determined by TLC comparison with authentic samples.

Compound **3a** mp 250 – 255℃. EI-MS *m/z* 486 $[M]^+$. ^1H NMR (C_5D_5N, 400 MHz): δ 0.79 (3H, s, H – 26), 0.86 (3H, s, H – 29), 0.97 (3H, s, H – 30), 0.99 (3H, s, H – 25), 1.12 (3H, S, H – 24), 1.38 (3H, s, H – 27), 5.26 (1H, br s, H – 16), 9.42 (1H, a, H – 23), 5.29 (1H, m, H – 12). ^1H and ^{13} NMR spectral data were identical to the published (Yoshikawa *et al*, 1991).

Compound **4** white amorphous powder. mp 232 – 235℃. $[\alpha]_D^{20}$ – 106.98° (c = 0.43, CH_3OH). FABMS *m/z*: 984 $[M]^-$ (100), 956 $[M-28]^-$ (65), 852 $[M-132]^-$ (15), 822 $[M-162]^-$ (10), 691 $[M-132-162]^-$ (8), 486 $[M-132-162-204]^-$ (3); HRFABMS: $[M-1]^-$ at *m/z*: 983.4832 (calcd for $C_{49}H_{75}O_{20}$, 983.4852). ^1H NMR (C_5D_5N, 400 MHz): δ 5.55 (1H, d, J = 7.7 Hz, Xyl – H – 1), 5.30 (1H, d, J = 7.8 Hz, Gal – H – 1), 4.88 (1H, d, J = 7.5 Hz, GlcUA – H – 1), 3.79 (1H, m, H – 3), 5.63 (1H, m, H – 12), 9.91 (1H, s, H – 23), 5.23 (1H, br s, H – 16), 1.39 (3H, s, H – 24); ^{13}C NMR data, see Table 1.

Table 1　^{13}C NMR spectral data for tunicosides A – D (**1 – 4**) in C_5D_5N (400 MHz)

Aglycone	1	2	3	3a	4	Sugar	1	2	3	4
1	38.2	38.2	38.1	38.0	38.1	GlcUA				
2	25.0	25.2	25.2	26.5	25.2	1	103.3	104.2	104.3	104.3
3	82.3	84.5	84.4	71.8	84.5	2	83.6	75.4	75.6	75.3
4	55.1	55.2	55.1	56.0	55.1	3	76.9	86.1	85.9	85.9
5	47.4	48.6	48.7	48.1	48.7	4	72.6	71.8	71.0	71.0
6	20.5	20.5	20.5	20.6	20.9	5	77.2	78.4	78.5	78.6
7	32.9	32.9	32.8	32.3	32.8	6	170.4	174.3	169.9	170.0
8	40.2	40.3	40.2	40.5	40.8	$O\underline{C}H_2CH_3$				61.4
9	47.1	47.1	47.1	46.8	47.1	CH_3	52.2		52.2	14.2
10	36.4	36.4	36.3	35.8	36.3	Gal				
11	23.6	23.9	23.8	23.3	23.6	1	106.3	103.6	103.8	103.9
12	122.1	122.2	122.1	123.6	122.1	2	74.4	73.7	73.7	73.7
13	145.3	145.3	145.3	145.1	145.3	3	75.0	74.8	74.7	74.7
14	41.5	41.6	41.5	41.9	41.5	4	70.2	70.4	70.3	70.2
15	36.2	36.2	36.1	35.5	36.2	5	77.6	76.8	76.8	76.8
16	74.7	74.8	74.7	74.6	74.2	6	62.3	62.0	61.9	61.9
17	48.9	49.0	49.0	48.7	48.7	Xyl				
18	41.5	41.6	41.5	41.8	41.5	1		104.9	105.0	105.0
19	47.4	47.4	47.3	46.5	47.3	2		75.3	75.3	75.2
20	31.1	31.1	31.0	30.6	31.1	3		78.6	78.6	78.6
21	36.3	36.4	36.3	36.3	36.2	4		70.9	70.8	70.8
22	33.0	32.9	32.8	32.7	32.8	5		67.3	67.7	67.4
23	209.4	210.5	209.8	207.6	210.0					
24	10.9	11.1	11.0	19.7	11.0					
25	15.8	15.8	15.8	15.8	15.7					
26	17.5	17.5	17.5	16.9	17.7					
27	27.3	27.3	27.2	27.1	27.2					
28	180.0	180.2	180.1	180.8	180.6					
29	33.4	33.5	33.3	33.6	33.4					
30	24.9	24.9	24.8	25.0	24.9					

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